DESIGN AND SYNTHESIS OF NEW MULTIFUNCTIONAL EUROPIUM MOLECULAR COMPLEX FOR OLEDS

A Report Submitted

for

Partial fulfilment Master of Science Degree

Under the Guidance of

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DECLARATION

I hereby declare that the project work entitled, ñ**DESIGN AND SYNTHESIS OF NEW MULTIFUNCTIONAL EUROPIUM MOLECULAR COMPLEX FOR OLEDS**ò submitted to NIT Rourkela, is an original work done under guidance of Dr. Vaidyanathan Sivakumar, Assistant Professor, Department of Chemistry, NIT Rourkela, and this project work is submitted in the partial fulfilment of the requirements for the award of Master of Science degree in Chemistry. The results incarnated in this thesis have not been submitted to any other institute for any other degree.

Date: 06/05/2014

(Ajit Kumar Pallei)

412CY2018

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THESIS CERTIFICATE

This is to certify that the thesis entitled ñ**DESIGN AND SYNTHESIS OF NEW MULTIFUNCTIONAL EUROPIUM MOLECULAR COMPLEX FOR OLEDS**ò submitted by **Mr. Ajit Kumar Pallei** to the National Institute of Technology, Rourkela for the award of degree of Master of Science is a bonafide record of research work carried out by her under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Rourkela 769 008 Research Guide

Date: 06/05/2014

Dr. V. SIVAKUMAR

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(Ajit Kumar Pallei)

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ABSTRACT

Key words: TPA-DPA, Fluorene, 1,10-Phenanthroline, ´-´* transition

Lanthanide based OLEDs are gained much importance due to their line like emission characteristics (f-f electronic transition) as well as phosphorescent visible range emission (IQE up to 100%). Most of the hole transporting materials reported are derived from aromatic amines, where the inclusion of arylamine units into the antenna should improve the hole injection/transporting properties of the Eu^{III}-phosphors. The present research work aim is to increase the internal quantum efficiency by using chromophore (fluorene) molecule in order to improve the ´-´* transition in the antenna and facilitate the energy transfer to europium ion, to link multi-functional ligands (TPA-DPA/ Fluorene and phenanthroline) that should be active as well as capable of charge transport. To fulfil this, a new efficient red emitting europium(III) molecular complex having neutral ligand [$Eu(TTA)_3$ (Phen-Fl-TPA-DPA) - $Eu(TTA)_3$ = Tris (thenoyltrifluoroacetone) Europium (III), Phen-Fl-TPA-DPA = N^1-(4-(diphenylamino)phenyl)-N^1-(4-(1-(9,9-diethyl-9H-fluoren-2-yl)-1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenyl)-N^4,N^4-diphenylbenzene-1,4-diamine) has been designed. The same has been successfully synthesised and optically characterised. The photophysical studies of the synthesized Ligand (Phen-FL-TPA-DPA) and Eu-complex have been carried out in the solution form by UV-Vis spectroscopy and spectrofluorimetry. The photoluminescence emission spectra of $Eu(TTA)_3$Phen-FL-TPA-DPA exhibits $^5D_0$-^7F_J (J=0-4) transitions of Eu(III) ion. The characteristic emission observed at 612 nm due to $^5D_0$-$^7F_2$ electric-dipole transition (non-centrosymmetric site). The thermogravimetric analysis (TGA) shows that the compound is thermally stable (278^{o}C (10%)) and it is good enough to fabricate the OLED device using the synthesised Eu(III)-complex.

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1. Introduction:

Light is a form of energy, another form of energy is required to get light. There are two common ways for the production of light is incandescence and luminescence [1].

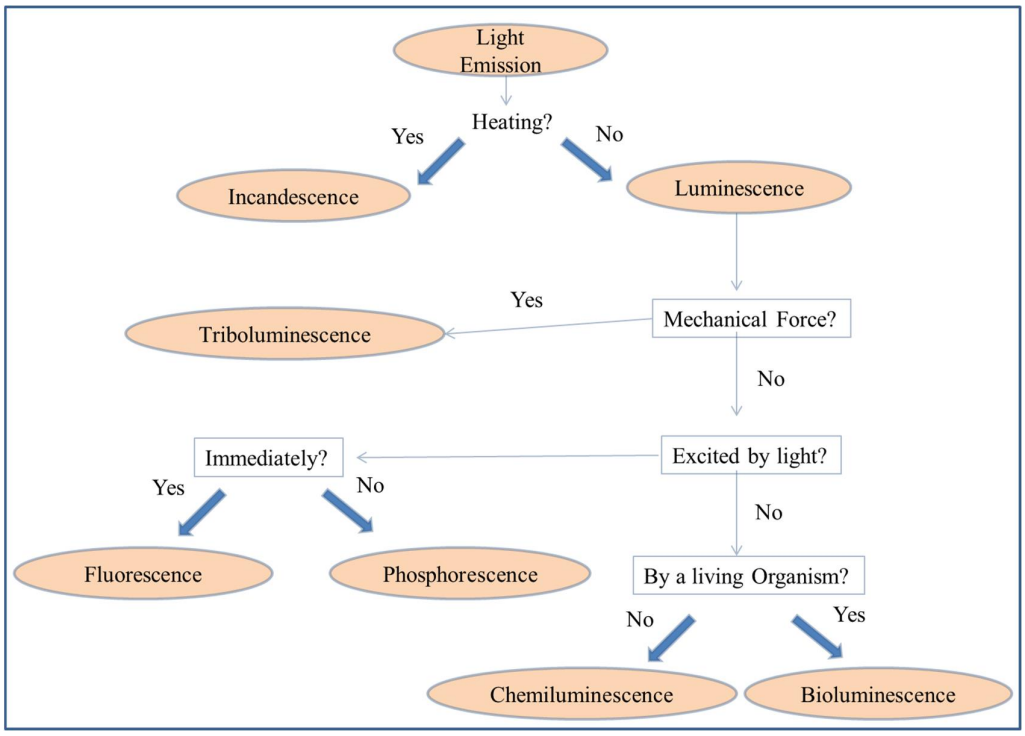


Fig. 1 Types of light based on source

1.1 Incandescence of light is nothing but heat energy. When heat something at high temperature, it will arise to glow. The metal in a flame begin to glow "red hot", that is incandescence. The tungsten filament of an ordinary incandescent light bulb is heated up to hotter, it glows brightly that is "white hot". It can see in sun and stars glow by incandescence [2].

1.2 Luminescence is also called as "cold light" that can be emitted at normal and lower temperatures. Luminescence is an emission of light it comes when the de-excitation of electron from the excited state to ground state i.e. when an electromagnetic radiation is applied to solid or gaseous materials excites the molecules and the substance glows. It have with few exceptions, the excitation energy is always greater than the energy (wavelength, color) of the emitted light. There are several varieties of luminescence, each named according to the source of energy, or the trigger for the luminescence [3]. The different types of luminescence process are mentioned in the table 1 based on their excitation source.

Table 1. Different types of luminescence

Type	Excitation Source	Example
Bioluminescence	Bio-chemical energy	firefly, Photinus pyralis
Cathodoluminescence	Cathode rays (high energy electrons)	microscopea
Chemiluminescence	Chemical reaction energy	luminol + hydrogen peroxide Ÿ 3-aminophthalate+ light
Electroluminescence	Applied voltage	OLEDs
Photoluminescence	Photons (UV, Visible)	
Radioluminescence	X-rays, ɔ rays, etc	Radium salt
Sonoluminescence	Sound waves	Bubbles in liquid
Thermoluminescence	Thermal stimulation of emission which is excited by some other means.	Sediment grains
Triboluminescence	Mechanical energy such as grinding, stress, etc.	Diamond

1.3 Triboluminescence is phosphorescence that is generated by mechanical action. This can observed when the breaking of chemical bands in a material.

1.4 Chemiluminescence is light, as a result of chemical reaction. Examples of chemiluminescencea are glow-in-the-dark plastic tubes sold in amusement parks.

1.5 Bioluminescence is luminescence caused by chemical reactions in living things; it is a form of chemiluminescence. Fireflies glow by bioluminescence.

1.6 Electroluminescence is luminescence caused by electric current [4].

The photophysical process of the molecule is explained in the Jablonsky diagram (Fig. 2)

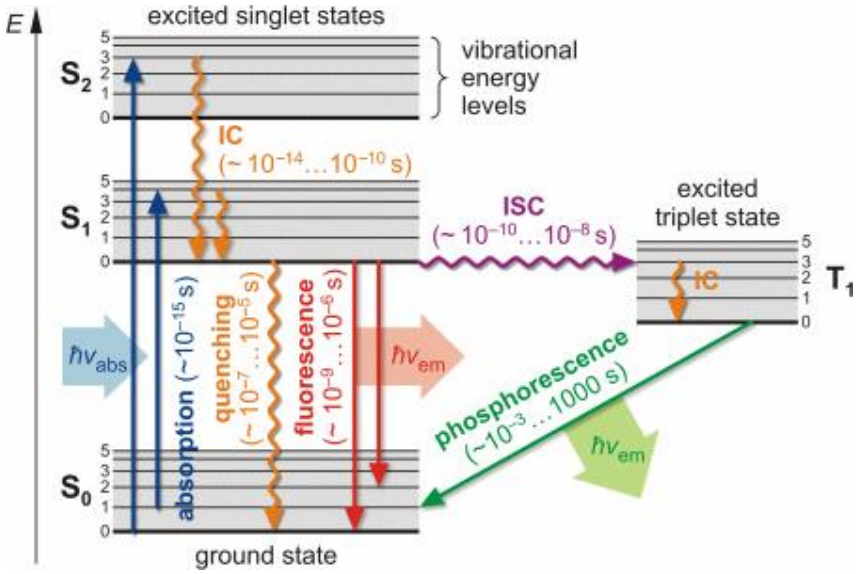


Fig. 2 Jablonski diagram

1.7 Fluorescence is the luminescence phenomena that occurred by supplying the energy in the form electromagnetic radiation, usually ultraviolet light. The energy source excites an electron of an atom from a lower energy level to an "excited" higher energy level and the same falls back to a lower energy level by emitting photon (i.e) what is known as fluorescence (s_1 to s_0) and it is allowed transition. The lifetime of an excited singlet state is approximately 10^{-9} to 10^{-6} sec. Examples: fluorescent lights, the red glow of rubies in sunlight [5].

1.7.1 Internal conversion is defined as radiationless processes where molecules in an excited singlet state return to the ground state without the emission of a photon, converting all the excitation energy into heat. The process called internal conversion. The life time of internal conversion is 10^{-14} to 10^{-10}. An example of this process is the quinine sulfate fluorescence, it quenched by the use of various halide salts. In this case the excited molecule can de-excite by increasing the thermal energy of the surrounding solvated ions.

1.7.2 Intersystem crossing is an isoenergetic radiationless transition between two electronic states having a different multiplicity that is singlet (S) to triplet (T). It can occur within the lifetime of an excited singlet state (10^{-10} to10^{-8} sec). It is facilitated by heavy metal ion (Ln metal ion).

1.8 Phosphorescence is defined as when a molecule is placed in a rigid medium where collisional processes are minimized, a radiative transition between the lowest triplet state and the ground state is observed. This emission is called phosphorescence (T_1 to S_0). The decay time of phosphorescence approximately equal to the lifetime of the triplet state (10^{-4} to 10 sec) as it originates from the lowest triplet state [6].

2. Lanthanides:

In the recent years development of lanthanide based luminescent materials are playing an important role due to f-f transitions. The excited states cannot be directly populated efficiently because of their forbidden nature transition. To improve their emission intensity requires a *sensitizer that can* populate the excited state manifold of the lanthanides by energy transfer (ET). Efficient intersystem crossing is required (heavy metal ion effect or spin orbit coupling). Mostly organic sensitizers have been used (due to their efficient absorption in the UV region). Energy matching of the sensitizer states to those of lanthanides are of exited states most importance [7] and the same in the pictorial view as shown in figure 3.

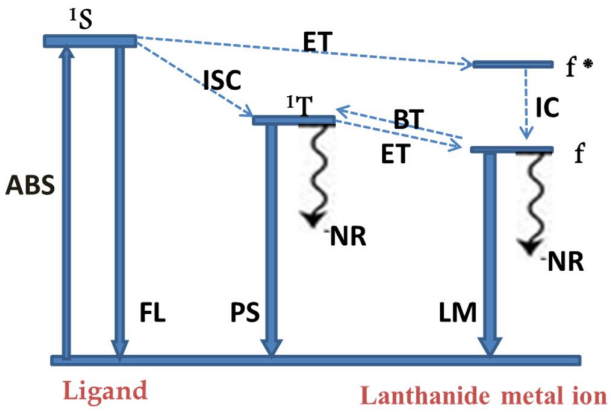


Fig. 3 Simplified mechanism for emission process

Lanthanides know as first inner transition series or third transition and come after lanthanum. Lanthanides are classified as f block elements. Generally these are called as rare earths. These are characterized by the filling up of the 4f energy levels which are not usually involved in bonding. These highly electropositive elements have a common oxidation state of +3 and generally resemble each other in their chemical and physical properties. They have a generic symbol ñLnò. It contains 15 elements from lanthanum (La_{57}) to lutetium (Lu_{71}) [8]. In the periodic table, covalent and ionic radii generally increase on descending a group due to the presence of extra filled shells of electron. When we go from left to right across a period, the covalent and ionic radii decrease. This is due to the extra orbital electrons incompletely shield

the extra nuclear charge. Thus the entire electrons are pulled in closer. The shielding effect of electron decreases in the order s > p > d > f. the contraction in size from one element to another is fairly small [9].

The photoluminescence properties of rare-earth (lanthanide) compounds have been attractive for researchers from decades. Line-like emission of lanthanide is an attractive feature of luminescent, which results in a high color purity of the emitted light. The emission color depends on the lanthanide ion and it is also depend on layers (HT/ET material) of the device which prefer to construct. Studies on these compounds have been limited to either inorganic compounds (lanthanide phosphors) or molecular lanthanide compounds (for instance, the ϐ-diketonate complexes). The study of luminescent lanthanide compounds are used for different a high potential applications (optical amplifiers, optical waveguides, OLEDs, etc.) [10]. Mostly the lanthanide materials are utilising for organic light emitting diodes (OLEDs) to produce visible range light emission.

2.1 Classic DiekeDiagram for Lanthanide ions

The classic Dieke diagram of lanthanide ions is shown in Fig. 4.

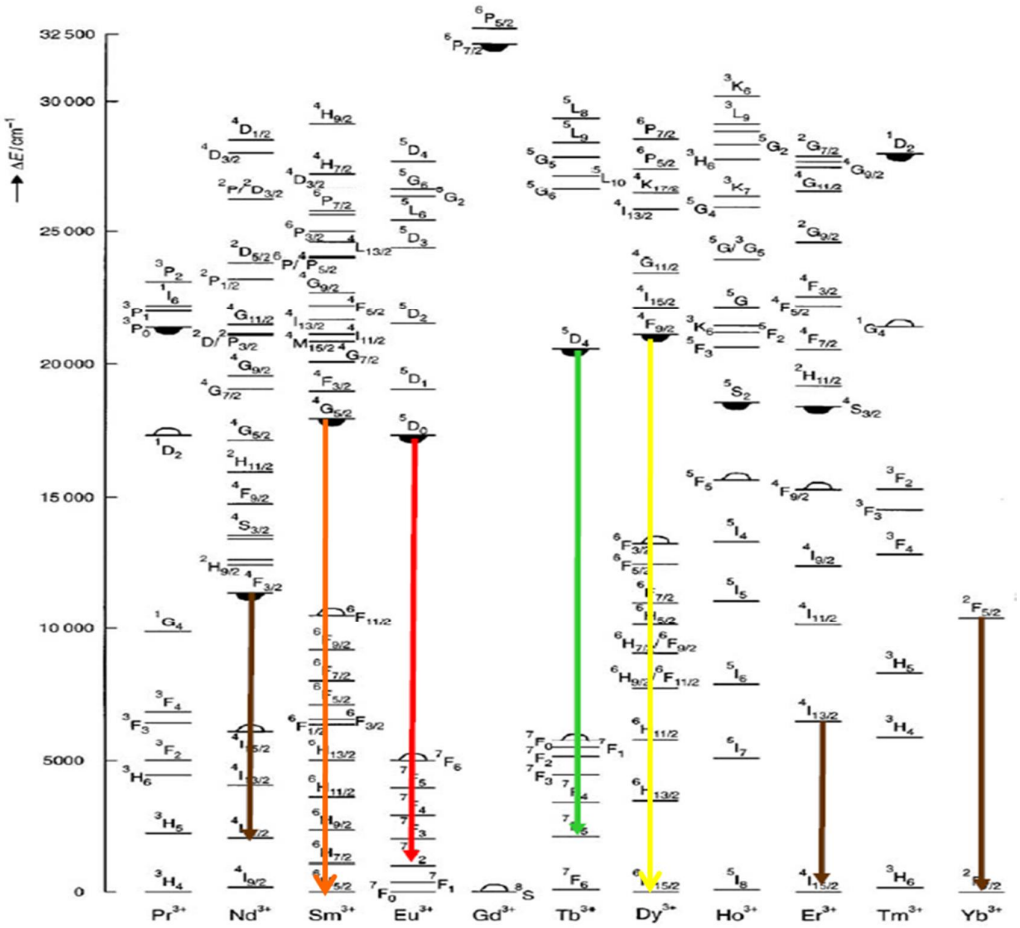


Fig. 4 Classic Dieke diagram

3. Organic light-emitting diode (OLED):

Organic light-emitting diode is a display device that sandwiches carbon-based films between two charged electrodes; those are cathode and anode respectively. The organic films consist of a hole-injection layer, a hole-transport layer, an emissive layer and an electron-transport layer. When the device is forward biased, electrons and holes moves from respective electrodes, cathode and anode (ITO). The injected charges are recombined at emissive layer to give emission in the form of light (EL). According to spin statistics the probability of forming singlet states is 25% and the triplet states is 75%. The maximum fluorescent QE is limited to 25% for the small organic molecule based OLEDs. To overcome the same Baldoet.al., introduced phosphorescent materials (expected to harvest the triplet energy to the ground state by light emission by spin orbit coupling, IQE can reach up to 100%) in the OLEDs [11]. In the absence of Ln (III) ion complexes, only singlet excitons are proficient to

give light emission but not the triplet excitons. Ln based organic metallic complexes incorporated in the emitting layer, both singlet and triplet excitons are utilized and which leads to increase in the device efficiency. The heavy metal ion effect facilitates the energy transfer from the singlet to triplet through ISC process and subsequently the emission arises from the f level [12].

3.1 History of OLEDs:

In 1907, Captain Henry Joseph Round was demonstrated inorganic luminescence on a crystal of carborandam [13]. Light emission from β-diketonates with lanthanide materials was first reported by Weissmanin 1942 [14]. The EL from organic material such as acridine orange has been observed first time by A Bernanose in 1955 [15]. In 1963 Pope reported single layer organic EL device with anthracene crystals [16] after that the Helfrich and Schneider also introduced single layer device [17]. In 1987, Tang and Vanshyke introduced high performance two layer OLED by vacuum deposition of organic layers have low bias voltage performance [18]. The dynamic work moved on OLEDs ofter this research work. In 1990, Burrougheset al., observed electroluminescence from organic polymer [19].In organometallic complex, ligand excitation energy is transferred to central metal ion through its triplet states and produce emission. In general blue, green and red colors are essential for full colour displays. Mixing of these colors produce the white color emission and it depends on host, HT, ET materials along with their appropriate voltages [20].

3.2 There are mainly two types of OLEDS are available. Those are

(1) Passive OLEDs (2) Active OLEDs

Table 2. Types of OLEDs

Passive OLEDs	Active OLEDs
➢ The organic layer is between strips of cathode and anode that run perpendicular ➢ The intersections form the pixels ➢ Easy to make ➢ Use more power ➢ Best for small screens	➢ Full layers of cathode and anode ➢ Anode over lays a thin film transistor (TFT) ➢ Requires less power ➢ Higher refresh rates ➢ Suitable for large screens

3.3 Architecture of OLEDs:

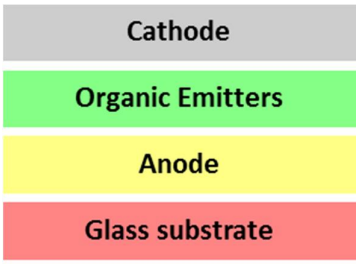


Fig. 5 OLED device structure

Substrate: clear plastic, glass, foil used as substrate in OLED.

Anode is source of holes. When a current flows through the device the holes will move from anode.

Organic emissive layer is made of organic material which is using in middle of the device.

Cathode is source for electrons. When a current flows through the device the electrons will move from cathode [21].

3.4 Advantages and Applications of OLEDs:

OLEDs are gained much importance due to their advantages such as longer life time, faster switching on smaller size, environment friendly, low cost, low drive voltages, colour purity and flexibility nature. Recently attractive results are reported on phosphorescent based Organic light emitting diodes (OLED) due to their internal quantum efficiency (up to 100%).

The Ln based organometallic complexes are used in different applications such as cathode ray tubes, Computer Screens, Keyboards, Digital Camera, air craft and space shuttles, television screens, fluoro immune assay, biomedicine and related technology, biophysical applications like receptors and sensing reagents of chiral biological substrates and photonic crystals, full colour flat panel displays [22-23].

Usually Eu(III) complexes exhibit red emission in the region around 614nm due to $^5D_0$-$^7F_2$ electronic transition (hyper sensitive). In order to obtain efficient emission, suitable designed molecules (multifunctional ligand) have to be chosen and the same have to be incorporated in suitable devices. In addition, the appropriate host materials have to be choosen and doping concentration need to be optimized. In the case of phosphorescent based OLEDs one can expect that the internal quantum efficiency (IQE) reach up to 100% (according to spin statistics). However, the external quantum efficiency (EQE) is not that satisfactory, efforts have been made to improve the EQE, and the different device structures have been

introduced. Charge carrier transportation and efficient recombination of the charge are more important for the device efficiency (EQE). Drift mobilities of charges (holes and electrons) in the device are strongly electric field and temperature dependent [24]. Lanthanide metal ions almost exhibit sharp-emission bands because of the 4f shell shielded by their outer orbitals. The Eu^{+3} metal ion shows 580, 592, 612, 652 and 703 nm emission lines corresponding f-f transitions of $^5D_0$-$^7F_0$, $^5D_0$-$^7F_1$, $^5D_0$-$^7F_2$, $^5D_0$-$^7F_3$ and $^5D_0$-$^7F_4$ (Fig. 6) [25].

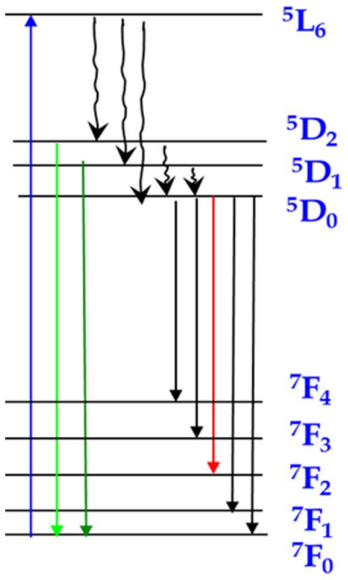
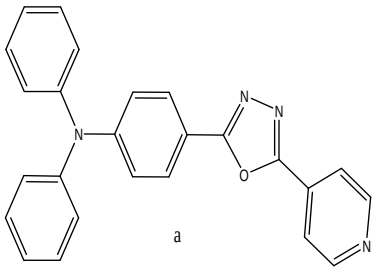


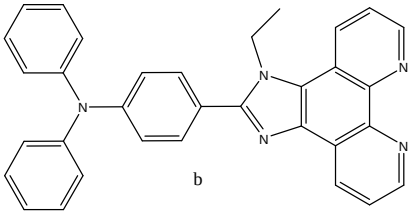
Fig. 6 Energy level diagram of Eu(III) ion

4. Bipolar ligands:

The ligand which is having both donor and accepter capacity is known as bipolar ligand.



N-phenyl-N-(4-(5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)phenyl)benzenamine



N-(4-(1-ethyl-1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenyl)-N-phenylbenzenamine

Fig. 7 Bipolar ligands a and b

The tittle compound, $C_{25}H_{18}N_4O$ (a), is a non-planar bipolar ligand containing triphenylamine and 1,3,4-oxadiazole units. In the molecule, the benzene ring, the 1,3,4-oxadiazole ring, and the pyridine ring are twisted slightly with respect to each other. It is well known that OLED produces light via recombination of electrons and holes, which are injected from electrodes on opposite sides of the device. Furthermore, the balance between the injection and transportation of electron and hole carriers leads to a high luminescence efficiency. Because triphenylamine and the 1,3,4-oxadiazol group possess good properties of hole transportation and electron deficiency, respectively, the compound containing these two groups should be of an increased electron affinity and transporting properties, resulting in a more balanced charge recombination in the emissive layer [26]. Tris(dibenzoylmethanato)(2-4ô-triphenylamino)imidazo[4,5-f]1,10 phenanthroline) is the light-emitting center, hole-transporting triphenylamine and electron-transporting phenanthroline fragments are integrated into one molecule [27].

Based on the extensive literature study, in the present investigation a bipolar ligand has been designed [multi functional ligand which is consist of phenanthroline, fluorene moiety and triphenylamine-diphenylamine] and the same is utilized as a bipolar ligand for the Eu molecular complex. The same is synthesized by the condensation of 1,10-phenanthroline-5,6-dione, 4-(bis(4-(diphenylamino)phenyl)amino)benzaldehyde (TPA-DPA) and 9,9-diethyl-9H-fluoren-2-amine.

5. Objectives of the work:

Although up to a great progress has been achieved in the development of green-emitters, full-color-displays also require red and blue-emitters. In accordance with the energy-gap law, the design and synthesis of efficient red emitters is intrinsically more difficult. Efforts have been made to design and synthesis europium based molecular complexes as a red emitting phosphor for OLEDs. From the literature survey we found these below tasks

(a) Design and synthesis of Eu based Lanthanide-luminophores (bright- monochromatic)

(b) Link the multifunctional ligands (Phen, Fl, TPA-DPA)

(c) Incorporate light-emitting luminophore (fluorene/β-diketone) in the antenna

(d) Fabricate Lanthanide-phosphors based OLEDs

(e) Improve the External Quantum efficiency (Above 5%)

6. Experimental Section:

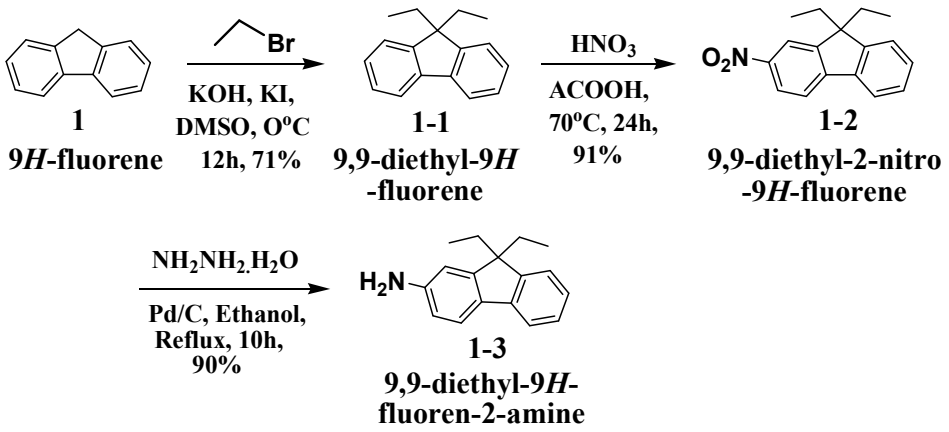
6.1 General Information for synthesis:

All reactions were performed under inert (nitrogen) atmosphere. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially (sigma Aldrich) available reagents are used without further purification unless otherwise stated. All the reactions was monitored by thin-layer chromatography (TLC) with silicagel 60 F254 Aluminium plates (Merk). Column chromatography was carried out using silica gel from Aldrich (70 ï 230 mesh, 60 Å).

6.2 Measurements:

^{1}H-NMR and ^{13}C-NMR spectra were recorded using a AV 400 Avance-III 400MHz FT-NMR Spectrometer Bruker Biospin International, Switzerland, in deuterated chloroform and deuterated dimethyl sulphoxide solution. Chemical shifts were quoted relative to tetramethylsilane (TMS). Elemental analysis was measured by Elementar Analysen Systeme, Germany/Vario EL. Mass spectra were recorded on an Perkin Elmer, USA/ Flexer SQ 300 M. The absorption spectrum was measured by using UV-visible spectrometer (Shimadzu Corporation, Japan/UV-2450 Perkin Elmer, USA/Lamda 25). Thermo gravimetry analysis were measured by DTA-Thermo Gravimetric Analyser (Shimadzu / DTG-60H).

6.3 Scheme of synthesis:



1 **9*H*-fluorene**

1-1 **9,9-diethyl-9*H*-fluorene**

1-2 **9,9-diethyl-2-nitro-9*H*-fluorene**

1-3 **9,9-diethyl-9*H*-fluoren-2-amine**

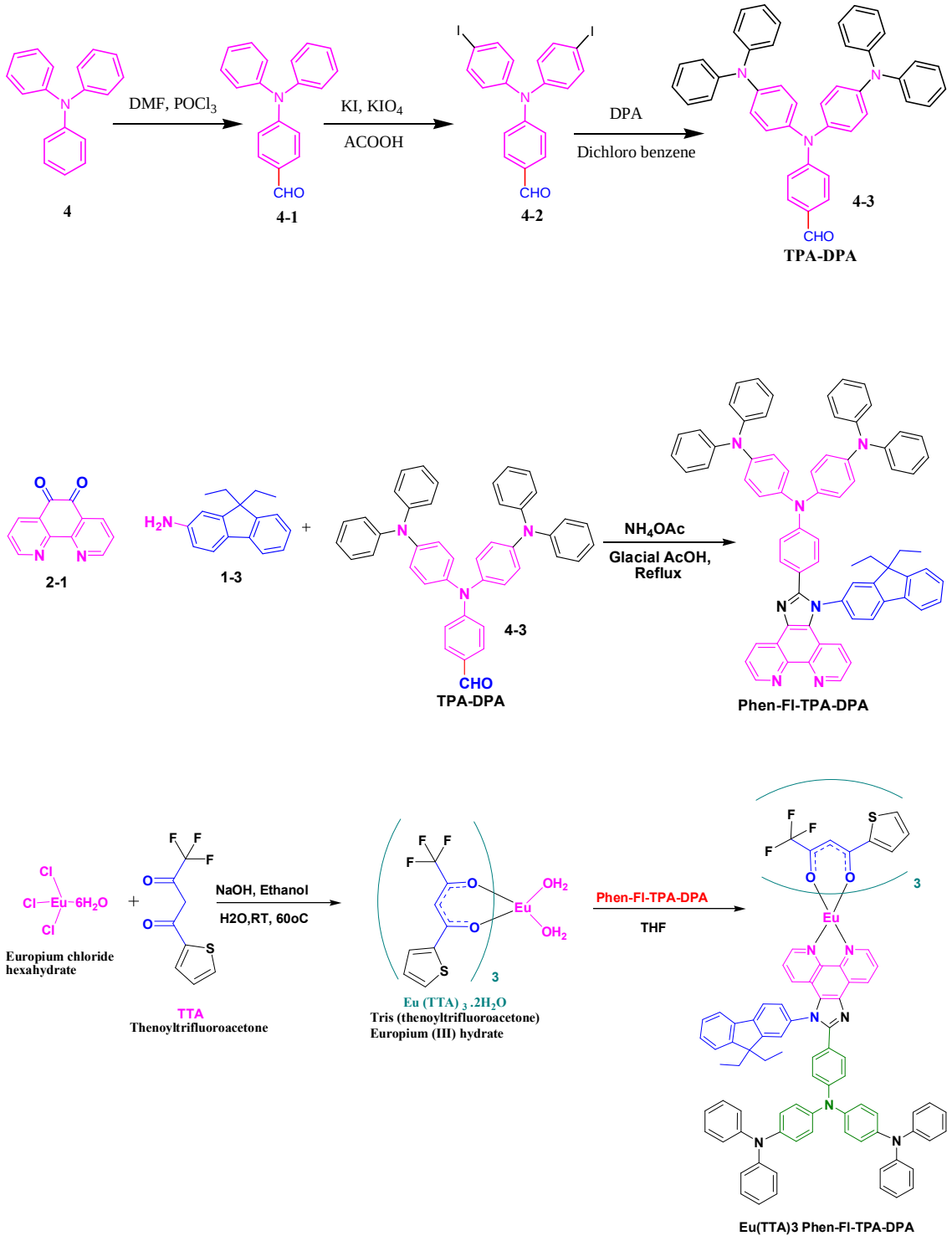


Fig. 8 Scheme of synthesis for designed new efficient red emitter [28-30]

6.4 Experimental Procedure:

1) Synthesis of 9,9-diethyl-9H-fluorene (1-1):

The powdered potassium hydroxide (KOH) (1.4g, 25.30mmol, 4.2eq) was added to a solution of Fluorene (1g, 6.024mmol, 1eq) in DMSO (25mL) and added 1-bromo ethane (0.97mL, 13.25mmol, 2.2eq) and KI (0.09g, 0.602mmol, 0.1eq) at O^{o}C. The reaction mixture (RM) was stirred for 12hrs at room temperature and the progress of the reaction was monitored by TLC (1:9 EtoAc: Hexane, Rf is 0.75). RM was pour into ice-cold water then extracted with chloroform (3×30mL). The combined organic layer was washed with brine and diluted hydrochloric acid (HCL) solution followed by drying with sodium sulphate, solvent evaporated to get 1.1g crude product with mixture of compounds. Purification carried out by using silica gel (100-200 mesh, EtoAc: Hexane 2:98) to a yield 1-1 a whitish color solid with 950mg (71%).

^{1}H-NMR Data ($CdCl_3$, 400MHz): δ 7.75-7.73 (m, 2H), 7.42-7.37 (m, 2H), 7.37-7.34 (m, 2H), 7.38-7.27 (m, 2H), 2.05 (q, 4H) and 0.34 (t, 6H).

2) Synthesis of 9,9-diethyl-2-nitro-9H-fluorene (1-2):

Into a clean two neck round bottom flask pour 1-1(0.2g, 0.899mmol) and added acetic acid (1.6mL) solution at RT. This mixture was heated to 50^{o}C then added nitric acid (0.2g, 5.411mmol) drop wise. The resulting mixture was stirred for 24hrs at 70^{o}C and the progress of the reaction was monitored by TLC (1:9 EtoAc: Hexane, Rf is 0.5). RM was cool to RT and poured into water then basified with diluted sodium hydroxide solution up to pH 6 (neutral), extracted with ethyl acetate combined organic layer was washed with brine followed by dried with anhydrous sodium sulphate, solvent was evaporated to get crude compound. This was washed with hexane and diethyl ether simultaneously to get 1-2 (220mg, 91%) with brick yellow color solid.

^{1}H-NMR Data ($CdCl_3$, 400MHz): δ8.29-8.15 (m, 3H), 7.81-7.74 (m, 2H), 7.47-7.35 (m, 2H), 2.10-2.06 (m, 4H) and 0.38-0.33 (m, 6H).

3) Synthesis of 9,9-diethyl-9H-fluoren-2-amine (1-3):

To a stirred solution of 1-2 (200mg, 0.749mmol) in ethanol (15 mL) added hydrazine monohydrate (0.5 mL) at RT. Then palladium on carbon (Pd/C, 10% w/w) (0.05g) was added under nitrogen atmosphere and resulting mixture was reflux (85^{o}C) for 10hrs. The progress of

the reaction was monitored by TLC (EtOAc: Hexane 2:8Rf is 0.6, ninhydrin active) and RM was filtered through celite bed followed by concentrated to get 190mg of 1-3 crude compound. This was purified with column chromatography by using silica gel (100-200 mash). The compound eluted with 8% ethyl acetate in pet ether and solvent concentrated to get 160mg (90%) 1-3 pure compound.

^{1}H-NMR Data ($CdCl_3$, 400MHz): δ 7.58-7.56 (m, 1H), 7.51-7.49 (m, 1H), 7.30-7.28 (m, 1H), 7.26-7.20 (m, 2H), 6.69-6.67 (m, 2H), 3.65 (bs, 2H), 2.03-1.91 (m, 4H) and 0.34 (t, 6H).

4) Synthesis of 4-(diphenylamino)benzaldehyde (4-1) :

Dimethylformamide (DMF) (1.71mL, 22.04mmol) was taken in a clean-dried two neck round bottom flask and added drop wise phosphorous oxy chloride (2.05ml, 22.04mmol) at 5^{o}C. After 30min, triphenylamine (TPA) (2g, 8.163mmol) in DMF (15mL) was added drop wise to reaction mixture at same temperature. The RM was appears in brick yellow color and the progress of the reaction was monitored by TLC (EtOAc in Hexane 1:9, Rf-0.4). The resulting mixture was stirred for overnight at RT, then poured into water and neutralized with diluted sodium hydroxide solution (up to pH 6). Then extracted with chloroform and washed with brine solution followed by dried with sodium sulphate and removal of solvent to get 2.2g of crude (4-1). The crude product was washed with diethyl ether: hexane (3:7) mixture solvent and recrystallization in ethanol to get 2g pure 4-(diphenylamino)benzaldehyde(4-1) (90%) with pale yellow colored fine solid.

^{1}H-NMR Data ($CdCl_3$, 400MHz): δ 9.82 (s, 1H), 7.70 (d, 2H), 7.38-7.34 (m, 2H), 7.25-7.24 (m, 2H), 7.20-7.15 (m, 6H), 7.03 (d, 2H).

^{13}C-NMR Data ($CdCl_3$, 100MHz): δ 153.3, 146.1, 131.3, 129.7, 129.0, 126.3, 125.1, 119.3. EI-mass: m/z 274 (M^++1)

5) Synthesis of 4-(bis(4-iodophenyl)amino)benzaldehyde (4-2):

Under rapid stirring, 4 (2.73 g, 10 mmol) was dissolved in glacial acetic acid (10 mL) and KI (3.32 g, 20 mmol) and KIO_3 (6.42 g, 30 mmol) were added; the reaction mixture was stirred for 3 h at 70^0 C. After cooling, the solid was filtered off and washed thoroughly with water (50 mL) and dichloromethane (100 mL). The aqueous phase was extracted several times with dichloromethane. The combined organic phases were washed with a diluted ammonia solution (10%) until pH becomes nearly 8, with a saturated $NaHCO_3$ solution, and with

saturated brine and dried over $MgSO_4$. After removal of the solvents, the crude compound was stirred for 15 min in boiling ethanol (50 mL); the solution was cooled, and the pure product was isolated by filtration (4.2 g, 80%). Yellow solid,

^{1}H-NMR Data (DMSO, 400MHz): δ 9.859 (s, 1H), 7.72 (d, 2 H), 7.64 (d, 4H), 7.07 (d, 2H), 6.91 (d, 4H).

6) Synthesis of 4-(bis(4-(diphenylamino)phenyl)amino)benzaldehyde (4-3) (TPA-DPA):

In a 250mL round bottom flask, 4-[N,N-di(4-iodophenyl)amino]- benzaldehyde (1g, 1.9mmol), diphenylamine (0.98g, 5.7mmol), potassium carbonate (2.09g, 15.2 mmol) copper iodide (0.28g, 1.52mmol) and 18 ï crown ï 6 (0.01g, 0.38mmol) were reflexed in 1,2 ï dichlorobenzene (15mL) for 48 hrs, under nitrogen atmosphere. The inorganic components are filtered while hot and then the product was precipitated in methanol. The crude product was purified by column chromatography on silica (petroleum ether: dichloromethane = 1:1, v/v) to afford the product as yellow powder (yield: 59 %).

1H-NMR Data (DMSO, 400MHz): δ 9.815 (s, 1H), 7.22 (t, 9H), 7.05 (d, 9H), 6.96 (d, 3H), 6.81 (t, 4H).

^{13}C NMR data (100MHz, DMSO-d_6): ŭ 190.97, 141.45, 140.82, 140.56, 140.15, 132.10, 130.02, 129.80, 127.91, 125.16, 125.11, 123.75, 115.40.

FT-IR Data (KBr): γ_{C-C} = 1501(aromatic), γ_{C-N} = 1308 (aromatic), $\gamma_{C-H\,(S)}$ = 695

7) Synthesis of N^1-(4-(diphenylamino)phenyl)-N^1-(4-(1-(9,9-diethyl-9H-fluoren-2-yl)-1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenyl)-N^4,N^4-diphenylbenzene-1,4-diamine (Phen-Fl-TPA-DPA):

1-3 (0.75g, 3.171mmol) was added to a stirred solution of 4-3 (1.75g, 2.883mmol) in glacial acetic acid (30mL) at room temperature. To this reaction mixture subsequently ammonium acetate (2.2g, 28.83mmol) and 2-1 (0.60g, 2.883mmol) was added. Then resulting mixture was stirred for 12hrs at 110^{o}C. The progress of the reaction was monitored by TLC (MeOH in Chloroform 1:9, Rf-0.2). The RM was pour into minimum amount of water and then ammonium hydroxide solution was added. Then the formed solid was filtered and dissolved in dichloromethane, followed by dried with anhydrous sodium sulphate and the solvent was evaporated to get 3g crude compound. The resultant compound was purified with column

chromatography by using silica gel (100-200 mesh), eluent with 5% methanol in chloroform and the solvent was evaporated and dissolved in minimum amount of THF solution added excess of hexane solvent, the pale yellow color solid was formed. After settled of solid, decant and repeated this process three more times and get compound- Phen-Fl-TPA-DPA, 1g solid.

^{1}H-NMR Data (CdCl3, 400MHz): δ 9.21-9.16 (m, 2H), 9.03 (d, 1H), 7.91 (d, 1H), 7.87-7.76 (m, 3H), 7.62-7.45 (m, 8H), 7.25-7.16 (m, 9H), 7.14-7.06 (m, 11H), 7.01-6.96 (m, 11H) 2.05 (q, 4H), 0.42 (t, 3H), 0.24 (t, 2H).

EI-mass: m/z 1019.24 (M^++1)

FT-IR Data (KBr): γ_{N-H} = 3426, γ_{C-H} = 3032 (aromatic), γ_{C-C} =1490 (aromatic), γ_{C-N} = 1310 (aromatic), $\gamma_{C-H\ (S)}$ = 695

8) Synthesis of Eu $(TTA)_3.2H_2O$:

Taken a 100 mL of two neck round bottom flask with balloon contained adaptor and poured TTA (Thenoyltrifluoroacetone) (1g, 4.504 mmol, 3eq) dissolved in absolute ethanol (20 mL) and then sodium hydroxide (0.186g, 4.650 mmol, 3.1eq) solution is added. Then the reaction mixture was stirred for 30min and Europium chloride hexahydrate ($EuCl_3.6H_2O$) (0.549g, 1.5 mmol, 1eq) solution added and after some time 50 mL of deionised water is added. The reaction mixture was stirred for overnight at 60^{o}C.

The yellowish white precipitate was observed and the precipitate was filtered, dried in vaccum. The obtained powder was dissolved in minimum amount of THF and then filtered through cotton filled pipette. Pentane layer is made in the clear THF solution and kept in the freezer for crystallisation. The purified compound is dried to get 0.95 g (74.8%)oftris (thenoyltrifluoroacetone) Europium (III) hydrateand used for further analysis.

^{1}H-NMR Data ($CdCl_3$, 400MHz): δ7.45 (s, 3H), 6.37 (d, 6H), 3.59 (s, 3H).

CHNS Analysis: Anal. Calc. for $C_{24}H_{16}EuF_9O_8S_3$: C, 33.85; H, 1.89; S, 11.30. Found: C, 33.60; H, 1.37; S, 10.89%.

FT-IR Data (KBr): γ_{C-O} = 1617 (aromatic), $\gamma_{C=C}$ =1539 (aromatic), γ_{C-N} = 1305 (aromatic).

9) Synthesis of $Eu(TTA)_3$ Phen-Fl-TPA-DPA:

Taken a 50mL two neck round bottom flask with nitrogen containing balloon contained adaptor and poured Eu $(TTA)_3.2H_2O$ (83g, 0.098mmol, 1eq) dissolved in dry tetrahydrofuron (THF) (10mL). The compound- Phen-Fl-TPA-DPA (100g, 0.098 mmol, 1eq) dissolved in THF (10mL) and added to stirred solution of reaction mixture (RM) then stirred for 12hrs at room temperature. The resulting mixture was concentrated and dissolved in minimum amount of THF and added excess of hexane to get solid product. After settled of solid, decant and repeated it another two times and dried to get pale yellow color solid with mg 150mg (84%). The obtained solid was dissolved in minimum amount of THF and then filtered through cotton filled pipette. Pentane layer is made in the clear THF solution and kept in the freezer for crystallisation.

EI-mass: m/z 1834.9 (M^++1)

CHNS Analysis: Anal. Calc. for: $C_{96}H_{67}EuF_9N_7O_6S_3$; C, 62.88; H, 3.68; Eu, 8.29; F, 9.32; N, 5.35; O, 5.23; S, 5.25%. , Found: C, 61.81; H, 3.08; Eu, 7.80; F, 9.85; N, 5.25; O, 5.01; S, 5.45.

FT-IR Data (KBr): γ_{N-H} = 3436, γ_{C-O} = 1600 (aromatic), γ_{C-C} =1501 (aromatic), γ_{C-N} = 1305 (aromatic), $\gamma_{C-H\,(S)}$ = 695

7. Results and Discussion:

The designed Eu-complex ($Eu(TTA)_3$ Phen-Fl-TPA-DPA) is successfully synthesised and characterised. The photophysical properties were measured with UV-Visible and spectrofluorimetry analysis. The thermogravimetric analysis (TGA) shows that the compound is thermally stable (278^oC (10%)) and it is good enough to fabricate the OLED device using the synthesised Eu(III)-complex.

The digital photographs was taken under long UV lamp (365 nm) for the corresponding Eu-complex and Eu $(TTA)_3$ and the same has been shown in Fig. 9.

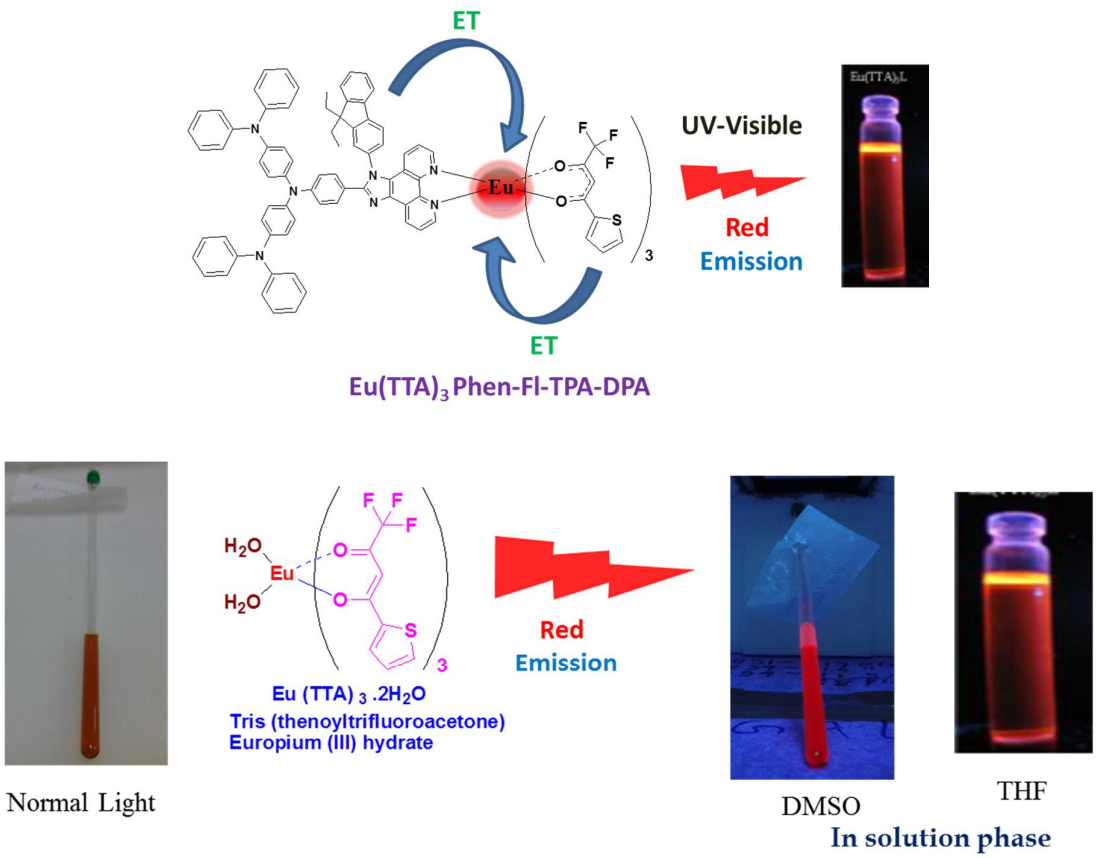


Fig. 9 Europium complex and $Eu(TTA)_3$ under normal light and UV-light (365nm)

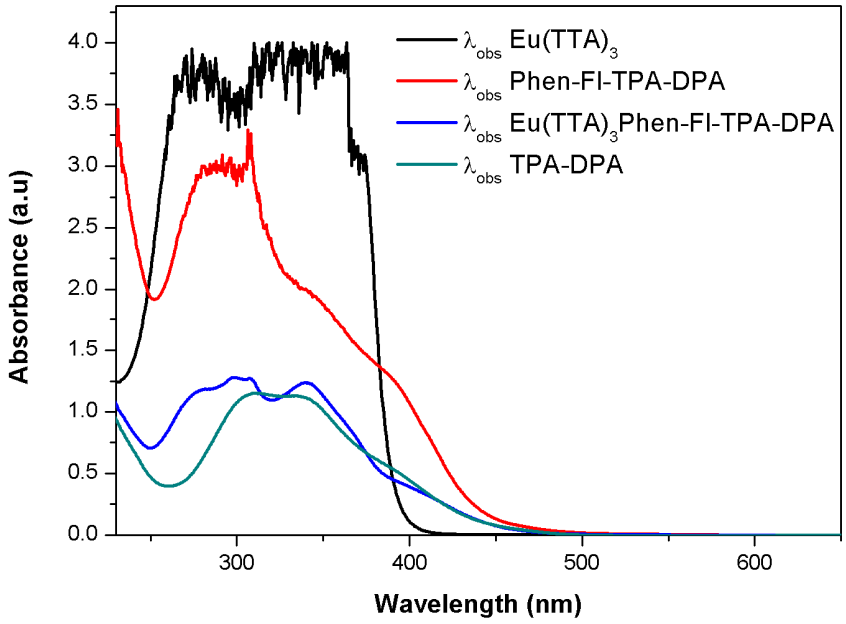


Fig 10. The UV-visible absorption spectra of Europium complex and $Eu(TTA)_3$ in chloroform solution (concentration 10^{-5}M).

The UV-visible absorption spectra of Ligand (L = Phen-Fl-TPA-DPA), Europium complex, and $Eu(TTA)_3$ in Dichloromethane solution (concentration is 10^{-5}M) is shown in Fig. 10. The absorption spectrum of Ligand shows absorption from 250 to 450 with λ_{max}. 360 nm, 275 nm, these bands were attributed to the ´ Ÿ ´* transitions of the ligands. Similarly the Eu $(TTA)_3$ Phen-Fl-TPA-DPA and Eu $(TTA)_3$ shows the peak maxima at 341nm, 278 nm and 340nm and 275nm, respectively. It indicating that the efficient energy transfer from the Ligand molecule to central Eu(III) metal ion.

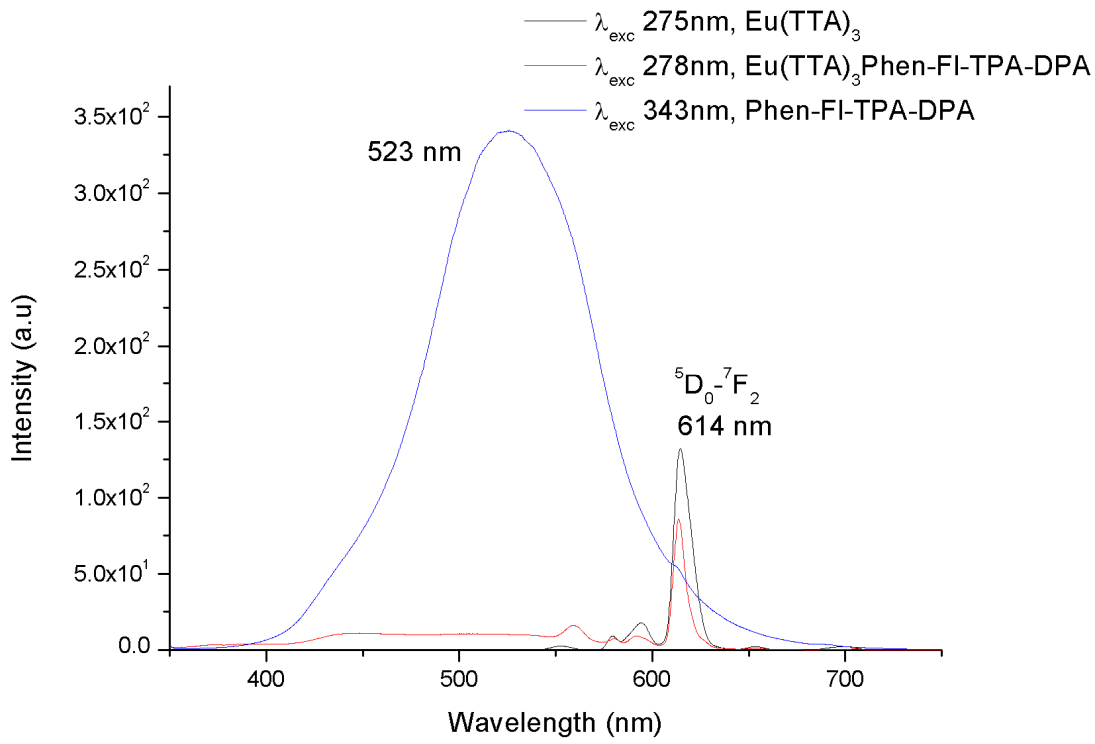


Fig. 11 The photoluminescence emission spectra of $Eu(TTA)_3.2H_2O$, $Eu(TTA)_3$Phen-FL-TPA-DPA and Phen-Fl-TPA-DPA

The photoluminescence emission spectra of $Eu(TTA)_3$Phen-FL-TPA-DPA exhibits $^5D_0$-$^7F_2$ (J=0-4) transitions of Eu(III) ion. The consist of $^5D_0$-$_7F_o$ transition (580nm, single peak) in the emission spectra indicates that the all Eu^{3+} ions occupy a site of the same symmetry and experience the same crystal field perturbation [31]. The most intense induced electronic dipole transition is $^5D_0$-$^7F_2$ observed at 614 nm and this intensity is sensitive to the chemical environment. The photoluminescence emission spectrum of ligand (Phen-FL-TPA-DPA) exhibits a broad emission peak at 523 nm due to TPA-DPA.

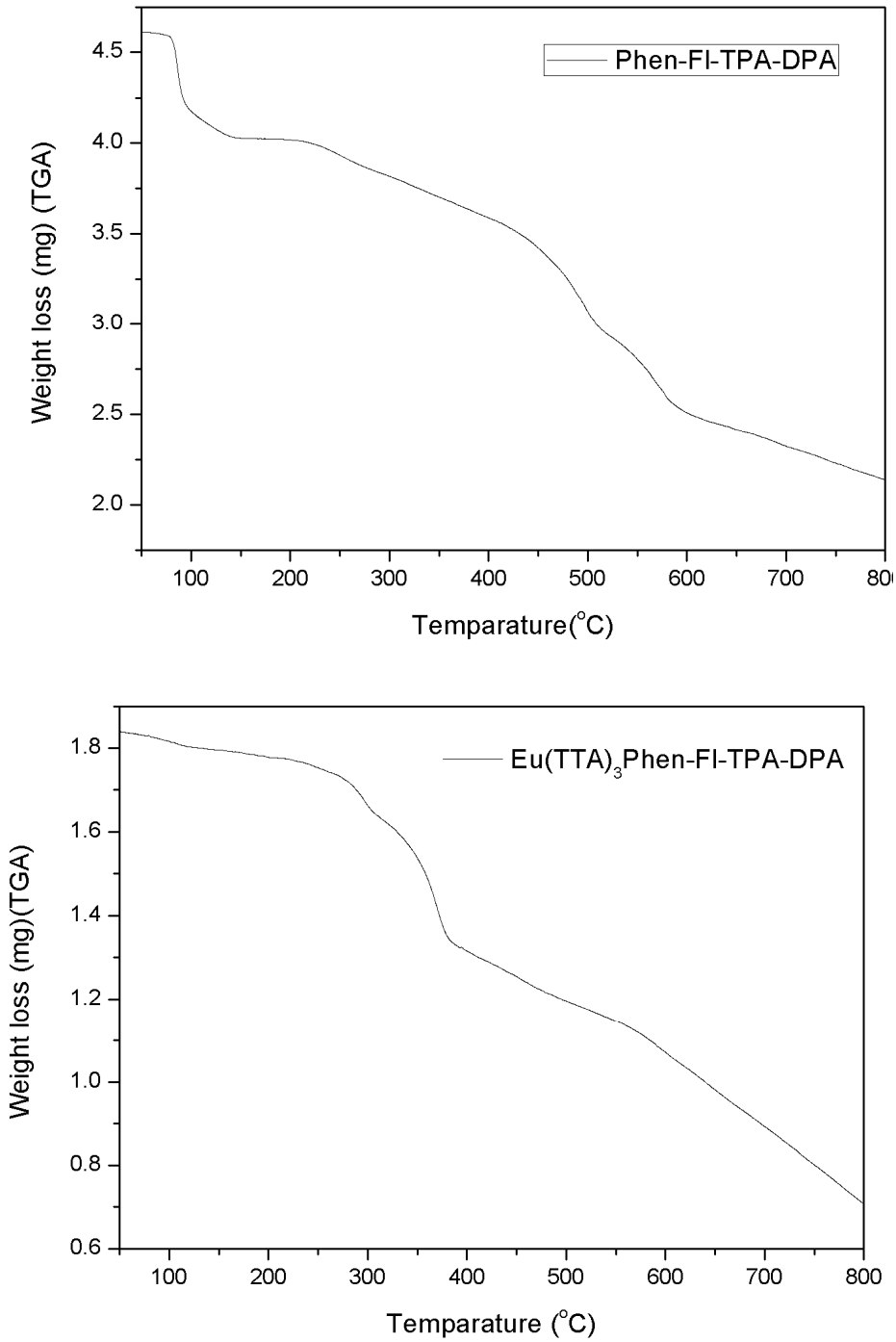


Fig. 12 Thermogravimetric analysis (TGA) for Phen-Fl-TPA-DPA and $Eu(TTA)_3$Phen-FL-TPA-DPA

The thermogravimetric analysis were measured under nitrogen atmosphere with 10°C per minute for Phen-Fl-TPA-DPA and $Eu(TTA)_3$Phen-FL-TPA-DPA (fig. 12). The compound Phen-Fl-TPA-DPA shown 20% thermal decomposition at 370°C and $Eu(TTA)_3$Phen-FL-

TPA-DPA shown 10% decomposition at 278^{o}C. These are indicating that synthesised Eu-Complex have above 250^{o}C decomposition. It is thermal stable enough to be fabricate device.

8. Summary and conclusions:

- The expected efficient red emitting molecular material based on Eu-complexes with charge-transporting antenna was successfully synthesized and characterized by NMR, Mass and elemental analysis.
- Form the UV-visible and PL spectral analysis, we observed that the efficient energy transfer from the Ligand molecule to central Eu(III) metal ion.
- TGA is shown thermal stable (278^{o}C (10%)) enough to be fabricate device.

9. Scope for the future work:

- The HOMO and LUMO levels of the ligand and the complexes will be determined by using cyclic voltammetry.
- Glass transition temperature will be determined by using DSC analysis.
- From the synthesised Eu-complex, it is expected that the TPA can transport the hole (HT) and phenanthroline can transport the electron (ET) in the OLED device
- The synthesised Eu(III)-complex will be incorporated with suitable OLED device structure.
- The electroluminescence properties of the proposed device will be measured.

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